Quadricyclanen en 3-Oxaquadricyclanen. Overgangsmetaal gekatalyseerde reakties en dynamische processen.

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SUMMARY

In the first part of this thesis are presented the results of a mechanistic study of transition metal- and acid-catalyzed isomerizations of quadricyclanes and 3-oxaquadricyclanes. The second part deals with dynamic processes undergone by [8](2,4)-1,5-dicarbomethoxy-3-oxaquadricyclane, [8](1,4)-7-oxanorbornadiene and di-[8](1,4)-7-oxanorbornadienerhodium chloride.

After the introduction of this work (Chapter 1) it is shown in Chapter 2 that substitution at C_3 in quadricyclanes has no substantial effect on either the rates or nature of the products of the $Rh_2(NOR)_2Cl_2$-catalyzed valence-isomerization of these compounds. However, introduction of two carbomethoxy substituents at C_1 and C_5 leads to an appreciable retardation of the valence-isomerization. Variation of the catalyst does not change the nature of the products; only the corresponding norbornadienes are formed. Furthermore, it is shown that the mechanism of the $Rh_2(NOR)_2Cl_2$-catalyzed isomerization is rather complicated as compared to that of the $Pd(C_6H_5CN)_2Cl_2$-catalyzed isomerization, and that the $AgClO_4$-catalyzed isomerization proceeds *via* ionic intermediates.

The transition metal-catalyzed reactions of 3-oxaquadricyclanes do not, in contrast to those of the quadricyclanes, lead to the corresponding 7-oxanorbornadienes. The products formed depend upon the catalyst used (Chapter 3): the $AgClO_4$-catalyzed reactions occur *via* two routes, both leading to the same reaction products (6-hydroxyfulvenes), as is shown by a kinetic analysis. In the $Rh_2(CO)_4Cl_2$-catalyzed reactions the main products (oxepines) arise from a Lewis acid-type reaction; byproducts (6-hydroxyfulvenes) in the $Rh_2(CO)_4Cl_2$-catalyzed reactions are the result of an oxidative addition-type reaction, as in the $Rh_2(NOR)_2Cl_2$- and $Pd(C_6H_5CN)_2Cl_2$-catalyzed reactions. The acid-catalyzed reaction occurs *via* attack at a cyclopropyl ring and not *via* initial protonation of the ether oxygen atom. It is found that the octamethylene chain in [8](2,4)-1,5-dicarbomethoxy-3-oxaquadricyclane (301b) dramatically affects both product formation ($AgClO_4$- and $Rh_2(CO)_4Cl_2$-catalyzed reactions) and rate (thermal decomposition and CCl_3COOH-catalyzed reaction).

The octamethylene chain of compound 301b undergoes two processes, which have been studied by ^{1}H-NMR spectroscopy (Chapter 4). The slower process involves the interconversion of the two conformers of 301b, which also exist in the solid state. In the faster process a conformational interchange of the octamethylene chain in each of the above-mentioned conformers takes place.

The octamethylene chains in [8](1,4)-7-oxanorbornadiene and di-[8](1,4)-7-oxanorbornadienerhodium chloride show analogous dynamic processes, which have been studied with NMR spectroscopy (Chapter 5). In di-[8](1,4)-7-oxanorbornadienerhodium chloride two additional processes have been observed: These are a degenerate one, probably involving a rotation of the 7-oxanorbornadiene ligands around the rhodium-oxygen axes), and a non-degenerate one involving an exchange of coordinated and free 7-oxanorbornadiene.

In Chapter 6 the experimental details of the work described in this thesis are given.